<Fundamental Material Properties> Molecular Rheology

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- Molecular Rheology -

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Dr Steve Granick — University of Illinois, USA, 2 December 2002

Scope of Research

The molecular origin of various rheological properties of materials is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluids while heterogeneous polymeric systems exhibit plasticity in addition to these features. For a basic understanding of the features, the molecular motion and structures of various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of autocorrelation of the orientation with dynamic dielectric spectroscopy.

Research Activities (Year 2002)

Presentations

Rheo-Dielectric Behavior of Entangled Chains: An Approach to Convective Constraint Release, H. Watanabe, UCSB ITP Workshop for Dynamics of Complex and Macromolecular Fluids, 23 April.

Coarse Grained Dynamics Investigated by Dielectric and Viscoelastic Relaxation, H. Watanabe, Nagoya University International Workshop on Coarse-Grained Dynamics in Soft-Materials, 28 June.

Rheo-Dielectrics in Oligomeric and Polymeric Fluids, H. Watanabe, Pisa University III Workshop on Non-Equilibrium Phenomena in Supercooled Fluids, Glasses, and Amorphous Materials, 24 September.

Birefringence and Viscoelasticity of Polymers around the Glass Transition Zone, T. Inoue, Pisa University III Workshop on Non-Equilibrium Phenomena in Supercooled Fluids, Glasses, and Amorphous Materials, 24 September.

Rheology of Poly(Methyl Methacrylate-co-Styrene) Particles Suspended in Water: Electrostatic Interaction and Brownian Motion, H. Watanabe, Y. Matsumiya, T. Kanaya, Y. Takahashi, M. Horigome, M. Yada, and A. Miyakawa, Japan-Korea-Australia Three Nation Conference on Suspension Rheology, 14 October.

Significance of the Longest Rouse Relaxation Time in the Stress Relaxation Process of Entangled Polymer Solutions, T. Inoue, and K. Osaki, Polymer Conference on the Mission and Challenges of Polymer Science and Technology, 4 December.

Grants

Watanabe H, Molecular rheology of amorphous polymer studied by electric birefringence, Grant-in-Aid for Scientific Research (B) (2), 1 April 2001 - 31 March 2003.

Inoue T, Molecular rheology of polymer solids, Grant-in-Aid for Scientific Research (C) (2), 1 April 2001 - 31 March 2003.

Matsumiya Y, Effect of branching and molecular weight distributions on entanglement relaxation, Grant-in-Aid for Scientific Research, 1 April 2001 - 31 March 2003.

Paul KRA, Development of a Model for Entanglement Dynamics of Polymers Having Multiple Coarse-graining Scales, Grant-in-Aid for Scientific Research, 1 April 2002 - 31 March 2004.

The former professor Kunihiro Ozaki retired on 31 March 2002.
*Promoted to professor on 1 January 2003.

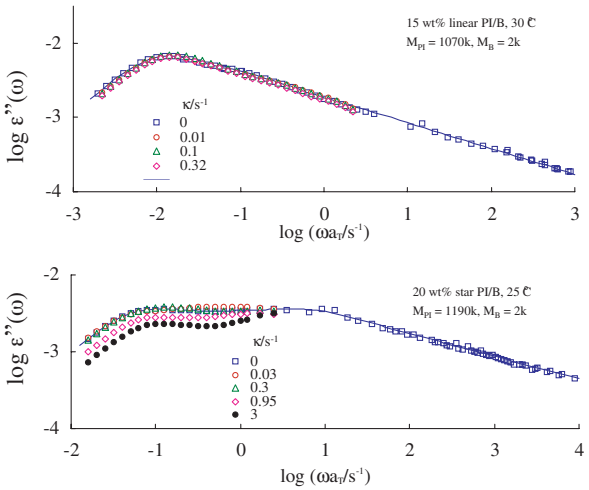
Dielectric Behavior of Entangled cis-Polyisoprene under Fast Shear.

Nonlinear relaxation is the most prominent feature of entangled polymer chains. A convective constraint release (CCR) mechanism, allowing the relaxation through a flow-induced chain motion, plays a central role in a recent molecular model [1]. This model describes the nonlinear viscosity (η) data fairly well, but the CCR picture assumed in the model has not been tested.

For this test, the dielectric loss ε"(ω) was measured at various angular frequencies ω for linear and six-arm star cis-polyisoprene (PI) chains under fast shear [2]: For these type-A chains, the dielectric relaxation frequency ω_ε and relaxation intensity Δε reflect the frequency of global chain motion and the chain size in the shear gradient direction, respectively.

For solutions of the PI chains in an oligomeric butadiene (B), the η data strongly decreased with increasing shear rate κ above the ω_ε at equilibrium (= 0.01 s^{-1} and 0.08 s^{-1} for the linear and star PI). However, the ε" data demonstrate just weak κ dependencies of ω_ε and Δε in particular for the linear PI; see Figure. The weak dependence of the chain size, seen through the Δε data, is attributed to a flow-induced orientational cross-correlation of the chain segments expected from the CCR picture [2]. However, the flow-induced acceleration of the chain motion (proportionality between κ and ω_ε) deduced from the simplest CCR picture is not observed experimentally. Thus, the current CCR model needs to be further refined.

1. S.T. Milner, T.C.B. McLeish, and A.E. Likhtman, J. Rheol., 45, 539 (2001).
2. H. Watanabe, S. Ishida, and Y. Matsumiya, Macromolecules, 35, 8802 (2002).



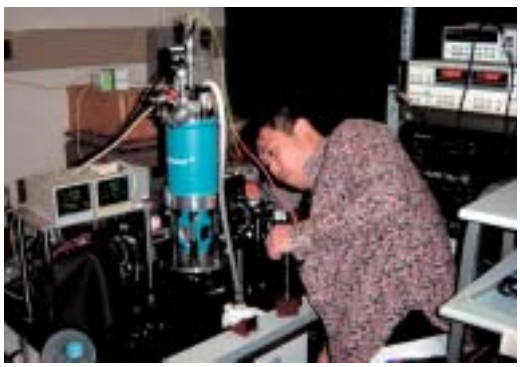
Dielectric loss of entangled cis-polyisoprene under shear flow. Upper panel: linear polyisoprene, lower panel: six-arm star polyisoprene. Dielectric loss of star polyisoprene at low frequencies is significanly suppressed by fast shear flow.

Electric Birefringence of amorphous polymers around the glass transition zone.

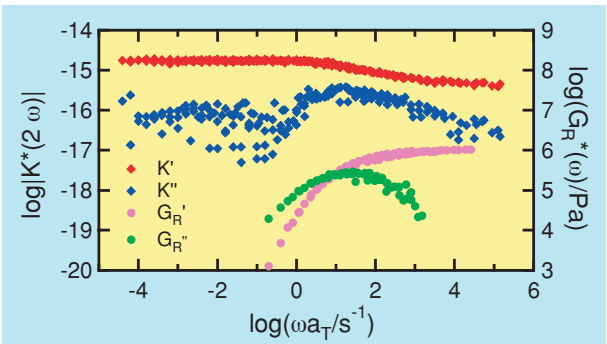
Amorphous polymers become anisotropic and birefringent when they are deformed. Reducing the strain induced birefringence is an important problem in processing of optical devices such as lenses and optical memory discs. We have shown that the strain induced birefringence can be related to the stress by the modified stress-optical rule, MSOR. The essence of the MSOR is the two molecular mechanisms (the chain orientation and twisting of the repeating units) that cause the birefringence.[1]

The MSOR is useful to understand the molecular dynamics of polymers around the glass transition zone.[2] Recently, we have measured electric birefringence of bulk polystyrene under oscillatory field. Comparing the chain orientation component of the shear modulus, we have found that the relaxation of the electric birefringence is mostly originated from chain reorientation. Thus, we have consistently explained all the relaxation processes of the electric birefringence, strain-induced birefringence, and modulus. The present result is easily extended to the reorientation of chain in the magnetic field, which is one of hot topics in the recent polymer science.

1. T. Inoue, H. Okamoto and K. Osaki, *Macromolecules*, **24**, 5670(1991).
2. T. Inoue and K. Osaki, *Macromolecules*, **29**, 1595(1996).



Measurement of electric birefringence by using a homemade apparatus.



Complex Kerr coefficient, $K^* = K' + iK''$, and chain orientation component of the shear modulus, $G_R^* = G_R' + iG_R'$, for bulk polystyrene (M = 1050). G_R^* was determined with the MSOR. Reference temperature is 298.15K.